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⑤④ **A process for the preparation of an oxirane compound.**

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GB-A- 1 602 460
US-A- 4 021 454
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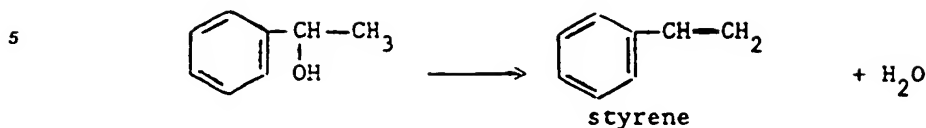
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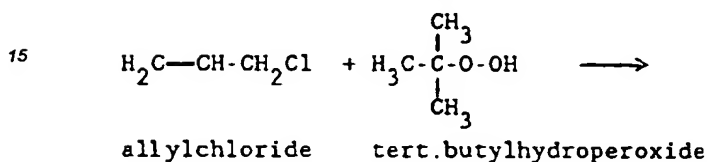
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step III:

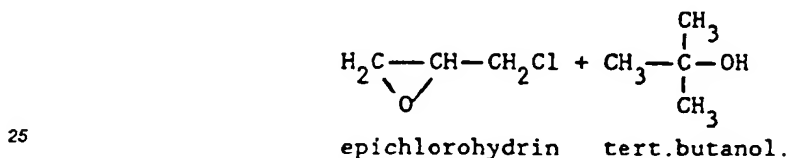


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Another reaction is for example:



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Applicant has now surprisingly found that in the preparation of the oxirane compound a much more active catalyst is used.

30 The invention relates to a process for the preparation of an oxirane compound by reacting an olefinic compound with an organic hydroperoxide by the use of heterogeneous catalyst, which is essentially insoluble in the reaction mixture, said catalyst comprising titanium in chemical combination with a solid silica and/or inorganic silicate characterized in that a catalyst is used obtainable by

- 35 a) impregnating the silicium compound with a stream of gaseous titanium tetrachloride,
 b) calcining the obtained reaction product of step a), and
 c) hydrolysis of the product of step b).

Preferably the preparation of the catalyst is performed in the presence of an inert gas, for example nitrogen which is inert under the reaction conditions. Other inert gases are for example carbon dioxide, argon, neon and helium. The inert gas has also the function of a carrier for the gaseous titanium tetrachloride. The titanium tetrachloride may react at rather low temperatures, but because of its low partial pressure the reaction will not be so fast. Therefore higher temperatures, above 130 °C are preferred.

40 Impregnation of the silicium compound with vaporized titanium tetrachloride proceeds smoothly at for example 180 °C. By a number of thermocouples during the impregnation in the silica or the silicate the temperature is measured and the reaction held under control. Sometime after the breakthrough of the gaseous titanium tetrachloride the supply of it is stopped.

45 Although the literature is not consistent how far the hydroxyl groups of the silicium compound have reacted with the titanium tetrachloride, it is a fact that the reaction product of step a) still contains too much chlorine in relation to titanium. Calcining the reaction product of step a) removes hydrogen chloride. Preferred calcination temperatures range from 400 °C to 900 °C. A more preferred temperature range is from 500 °C to 700 °C.

50 Without being bound to any theory, it is believed that the titanium tetrachloride reacts as follows with the silica compound:

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particular a secondary or tertiary alkyl or aralkyl group, having from 3 to 10 carbon atoms. Especially preferred among these groups are the tertiary alkyl and secondary or tertiary aralkyl groups, including, e.g., tertiary butyl, tertiary pentyl, cyclopentyl, 1-phenylethyl-1, 2-phenylpropyl-2 and the various tetralinyl radicals which originate by elimination of a hydrogen atom from the aliphatic side-chain of the tetralin molecule.

5 Aralkyl hydroperoxide, wherein the hydroperoxy group is linked to that carbon atom of an alkyl side-chain which is attached directly to an aromatic ring, including 1-phenylethyl-1-hydroperoxide and 2-phenylpropyl-2-hydroperoxide, are often called after the corresponding hydrocarbons, e.g. ethyl benzene hydroperoxide and cumene hydroperoxide. It will be appreciated that, when using ethylbenzene hydroperoxide, the resulting hydroxyl compound is 1-phenylethanol-1, also to be called methyl phenyl carbinol, which may be dehydrated to
10 styrene, and that, when using cumene hydroperoxide, the resulting hydroxyl compound is 2-phenylpropanol-2, also to be called dimethyl phenyl carbinol, which may be dehydrated to alpha-methylstyrene. Of course, both styrene and alpha-methylstyrene are industrially useful products.

Tertiary amines, which are useful as isoprene precursors, may be obtained by dehydration of the alcohol, which is formed when using tertiary pentyl hydroperoxide.

15 The organic hydroperoxide reactant used as a starting material may be in a dilute or concentrated, purified or unpurified condition.

In principle, any organic compound having at least one olefinic double bond may be reacted with an organic hydroperoxide. The compound may be acyclic, monocyclic, bicyclic or polycyclic and they may be mono-olefinic, diolefinic or polyolefinic. If there are more than one olefinic linkages, these may either be conjugated or
20 non-conjugated. Generally preferred are olefinic compounds having from 2 to 60 carbon atoms. Although substituents, which should preferably be relatively stable, may be present, acyclic mono-olefinic hydrocarbons having from 2 to 10 carbon atoms are of particular interest. Such hydrocarbons include, e.g., ethylene, propylene, isobutylene, hexene-3, octene-1 and decene-1. Butadiene may be mentioned as an example of a suitable diolefinic hydrocarbon. Substituents, if present, may, e.g., be halogen atoms or comprise atoms of oxygen, sulphur and nitrogen together with atoms of hydrogen and/or carbon. Of particular interest are olefinically unsaturated alcohols, and halogen-substituted olefinically unsaturated hydrocarbons, including, e.g., allyl alcohol, crotyl alcohol and allyl chloride. Particularly preferred are alkenes having from 3 to 40 carbon atoms, which may or may not be substituted with a hydroxy or a halogen atom.

Oxirane compounds are materials of established utility and many are chemicals of commerce, in particular
30 olefin oxides such as, e.g., ethylene oxide and propylene oxide. Propylene oxide may be converted into useful polymeric products by polymerization or copolymerization. Of commercial interest is also epichlorohydrin which may be obtained from allyl chloride and may, if so desired, be converted into glycerol. Of course, glycerol may also be made from the oxirane compound which is formed when starting from allyl alcohol.

Now, the present invention relates to the use of a specifically prepared catalyst composition which is essentially insoluble in the epoxidation reaction mixture, thus providing a heterogeneous system. It has surprisingly
35 been found that the catalyst composition of the invention is very active, and leads to high conversions of the organic hydroperoxide(s) introduced with high selectivities to the oxirane compound(s) concerned, these selectivities being defined as the molar ratios of oxirane compound(s) formed to organic hydroperoxide(s) converted.

In general, the epoxidation reaction is conducted in the liquid phase using solvents and/or diluents which
40 are liquid at reaction temperature and pressure, and substantially inert to the reactants as well as to the products. The presence of reaction materials such as, e.g., water is desirably avoided. A substantial part of the solvent may consist of materials present in the hydroperoxide solution employed. Preferred solvents further to be added are mononuclear aromatic compounds, e.g., benzene, toluene, chlorobenzene, bromobenzene, orthodichlorobenzene, and alkanes, e.g. octane, decane and dodecane. However, an excess amount of the
45 olefinic reactant may also serve as a solvent together with the solvent material introduced together with the organic hydroperoxide, so that no addition of any further solvents is needed. In most instances, however, added solvent is used. The total amount of solvent material may be up to 20 moles per mole of the hydroperoxide.

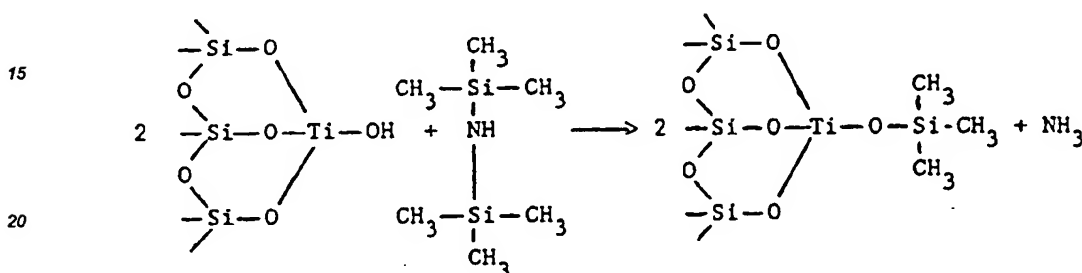
The epoxidation reaction, generally, proceeds at moderate temperatures and pressures, in particular at temperatures in the range of from 0 °C to 200 °C, the range from 25 °C to 200 °C being preferred. The precise
50 pressure is not critical so long as it suffices to maintain the reaction mixture in a liquid condition. Atmospheric pressure may be satisfactory. In general, pressures are suitably in the range of from 100 to 10000 kPa.

At the conclusion of the epoxidation reaction, the liquid mixture comprising the desired products may easily be separated from the solid catalyst material. The liquid mixture may then be worked up using any suitable conventional methods, including, e.g., fractional distillation, selective extraction and filtration. The solvent, the
55 catalyst and any unreacted olefin or hydroperoxide may be recycled for further utilization. The process of the invention can successfully be carried out with the catalyst in the form of a slurry, of a moving bed or a fluidized bed. However, a fixed catalyst bed is preferred for large-scale industrial operation. The process may be carried out in a batch-wise manner, semi-continuously or continuously. The liquid containing the reactants may then

ducted over the silica bed. After termination of the TiCl_4 distillation, dry nitrogen was led over the silica bed for 0.5 hour at 180 °C and at a rate of 20 l per hour.

The impregnated silica was then heated in a nitrogen atmosphere to 600 °C (at a rate of 50 °C/h) and calcined for 4 hours at 600 °C. The calcined silica/titania catalyst was cooled to 300 °C and steam was added to the circulating nitrogen which flowed at a rate of 20 l per hour over the catalyst. Steam treatment was carried out for two hours. The amount of steam was 12% by weight of the amount of nitrogen led over the catalyst.

The reactor was then cooled to 200 °C in a stream of dry nitrogen and hexamethyldisilazane was conducted over the catalyst bed for two hours using dry nitrogen as a carrier gas. An exotherm of 30 °C was observed, indicating a reaction of hexamethyldisilazane with hydroxyl groups in the catalyst. Excess of hexamethyldisilazane was stripped with nitrogen. Without being bound any theory, it is believed that the silylation reaction proceeds as follows:



Preparation of oxirane compound

The catalyst performance was tested in a tubular reactor which contained a catalyst as prepared above.

The epoxidation of propene was carried out with ethylbenzene hydroperoxide. A reaction mixture of about 6 mol propene per mol ethylbenzene hydroperoxide in ethylbenzene was continuously led through the reactor, with a liquid hourly space velocity of 5.58 h⁻¹. At 200 hours of operation the following conditions applied: Ethylbenzene hydroperoxide conversion was kept at 95.3 mol% by regulation of the temperature. The propene feed rate was 47.2 g per hour. The ethylbenzene hydroperoxide/ethylbenzene feed rate (27% mol/mol) was 96.6 g per hour. The propene/ethylbenzene hydroperoxide molar ratio was 5.98. The reaction temperature was 60 °C. The selectivity (to propylene oxide) was 95.9%.

EXAMPLE (Comparative)

A titanium silica catalyst, prepared by impregnation of silica with a solution of tetraisopropylorthotitanate, complexed with acetylacetone in isopropylalcohol and by silylation with hexamethyldisilazane, was also tested. Under comparable conditions after 200 hours of operation only the temperature was different, viz. the reaction temperature was 90 °C.

Since the activation energy for the reaction is 50 kJ/mol and since a temperature difference of 30 °C was measured the conclusion is that the catalyst used in the process according to our invention is 4.5 times as active as the catalyst used in the prior art process.

Claims

1. A process for the preparation of an oxirane compound by reacting an olefinic compound with an organic hydroperoxide by the use of a heterogeneous catalyst, which is essentially insoluble in the reaction mixture, said catalyst comprising, titanium in chemical combination with a solid silica and/or inorganic silicate characterized in that a catalyst is used obtainable by

- a) impregnating the silicium compound with a stream of gaseous titanium tetrachloride,
- b) calcining the obtained reaction product of step a), and
- c) hydrolysis of the product of step b).

2. A process as claimed in claim 1 wherein the catalyst before use is brought into contact with a silylating agent at elevated temperature.

3. A process as claimed in claim 1 or 2 wherein the preparation of the catalyst is performed in the presence of an inert gas.

zane.

9. Un procédé selon l'une des revendications 2 ou 8, dans lequel la température de silylation est comprise entre 100°C et 425°C.

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